Assessment of Heavy Metal Contamination in the Düzce Watershed (Türkiye) and Sustainable Remedies Through Aquatic Flora

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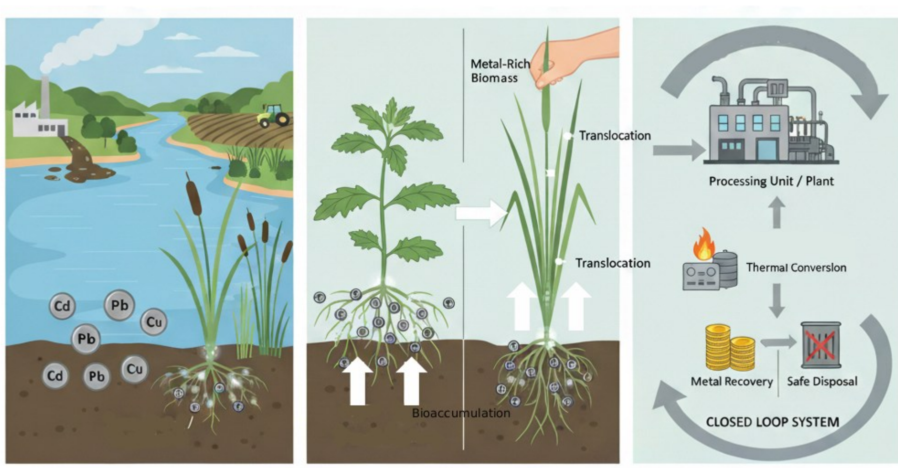
GRAPHICAL ABSTRACT



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Heavy metal pollution in the Düzce watershed of Türkiye was assessed and the phytoremediation potential of native aquatic plants was evaluated. The majority of heavy metals were found in water within legal limits, except for cadmium concentrations, which exceeded water quality standards; the main pollution load was accumulated in bottom sediments. Dominant wetland plants were analyzed to establish species-specific and tissue-specific metal accumulation patterns. Key species included *Plantago major* and *Paspalum distichum* with impressive copper accumulation capacity that may possibly classify them as good candidates for biomonitoring and phytoremediation applications. The results scientifically substantiate the use of local aquatic vegetation for ecological restoration efforts throughout Türkiye and similar regions as it pertains not merely to pollution mitigation but also a circular economy *via* the metal-accumulating plant biomass, which can serve these species afterward as sustainable resources for bioenergy production and biobased materials after phytoremediation activities. This brings forth new approaches to thinking about cleaning up an environment while recovering resources from polluted water ecosystems at the same time.

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Keywords: Heavy metal; River pollution; Phytoremediation; Macrophytes; Sustainable materials

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INTRODUCTION

Cu (copper), Cd (cadmium), Cr (chromium), Pb (lead), Fe (iron), and Zn (zinc) are heavy metals whose persistence, toxicity, and propensity for bioaccumulation present a pervasive global environmental challenge (Isinkaralar *et al.* 2024; Sevik *et al.* 2024; Isinkaralar *et al.* 2025; Koç *et al.* 2025a). In contrast to organic contaminants, heavy metals do not undergo microbial or chemical degradation; they remain in the environment and biomagnify through the food chain, thereby presenting substantial carcinogenic and mutagenic risks to aquatic ecosystems and human health (Liu *et al.* 2022). Consequently, remediation of waters contaminated with heavy metals has emerged as an urgent priority for global environmental protection and public health (Niampradit *et al.* 2024). Most metal pollution originates from human activities, encompassing industrial effluents, agricultural runoff, and mining operations (Zhang *et al.* 2015; Guan *et al.* 2018; Key *et al.* 2022; Koç 2025). Each element presents distinct risks and sources. Cd, which is frequently released from phosphate fertilizers and batteries, exhibits high toxicity even at low concentrations, leading to renal damage and bone demineralization in humans and animals (Genchi *et al.*

2020). Pb, primarily linked to battery production, vehicle emissions, and industrial paints, functions as a potent neurotoxin that hinders cognitive development in children and induces hematologic disorders (Wani *et al.* 2015). Cr, largely discharged from tanneries and metal plating facilities, is carcinogenic in its hexavalent state and can provoke respiratory and dermatological diseases (Costa and Klein 2006). Although Cu and Zn are essential micronutrients, they can become toxic at elevated concentrations (Ateya *et al.* 2023; Guney *et al.* 2023). Excess Cu, commonly attributable to fungicides and electronic waste, may cause liver cirrhosis and gastrointestinal distress (Al-Fartusie and Mohssan 2017). Similarly, elevated Zn levels, arising from galvanized surfaces and tire wear, can disrupt immune function and induce anemia (Plum *et al.* 2010). Ni, released from electroplating and fossil fuel combustion, is a known allergen and carcinogen that affects the respiratory and nasal tissues (Al-Fartusie and Mohssan 2017). Finally, although Fe is plentiful in the environment, excessive inputs from steel industry effluents can disrupt aquatic biodiversity by altering water turbidity and promoting bacterial growth that depletes dissolved oxygen (Vuori 1995; Al-Fartusie and Mohssan 2017).

Aquatic plants play a critical role in the proper functioning of ecosystems. They provide oxygen, participate in nutrient cycles, create habitats, and stabilize sediments, thus contributing to the water's natural self-cleaning processes. For this reason, macrophytes are considered biomonitors that can accurately reflect heavy metal pollution in water reservoirs (Miretzky *et al.* 2004; Tan *et al.* 2023). A substantial body of studies in river and lake environments has identified elevated accumulations of heavy metals. Studies have shown that heavy metal accumulation in aquatic plants can exceed the concentrations in the surrounding water by several times (Flefel 2020; Pillai 2020). However, element accumulation can vary significantly not only between species but also between different plant organs (roots, stems, *etc.*) and depending on the vegetation period (Eid *et al.* 2020; Tan *et al.* 2023). Traditional physicochemical treatment methods developed for managing heavy metal contamination are often unsustainable due to their high costs and energy intensity (Atasoy 2024). Consequently, there is a growing need for environmentally friendly and cost-effective biological alternatives. Among these alternatives, phytoremediation, which is based on the principle of plants removing heavy metals from the environment by accumulating them in their roots and tissues, stands out due to its tangible successes (Ma *et al.* 2019; Apori *et al.* 2020). Phytoremediation strategies have employed a wide range of plant species, from woody trees such as *Populus nigra* and *Pinus nigra* (El-Mahrouk *et al.* 2020; Şevik *et al.* 2024; Punitha *et al.* 2025) to aquatic macrophytes in wetland ecosystems. This method, carried out through aquatic macrophytes, has the potential to offer a simple and self-sustaining solution for the restoration of contaminated water sources (Stonkutė 2021; Mohebi and Nazari 2021). Heavy metal contamination represents a major global environmental challenge owing to its persistence, toxicity, and propensity for bioaccumulation. Unlike organic pollutants, heavy metals do not undergo microbial or chemical degradation; they remain in the environment and can biomagnify through food chains, thereby presenting substantial carcinogenic and mutagenic risks to aquatic ecosystems and human health (Liu *et al.* 2022). Consequently, the remediation of water bodies contaminated with heavy metals has emerged as an urgent priority for global environmental protection and public health (Niampradit *et al.* 2024).

Düzce Province is characterized by industrial establishments operating in various sectors such as metal-machinery, textiles, forest products, and mining (Düzce Governorate 2025). Therefore, the rivers and wetlands of Düzce Province are at risk of heavy metal pollution. However, riparian and wetland ecosystems also harbor communities of phytoremediation aquatic macrophytes with the potential to mitigate pollution. This study evaluates heavy metal pollution in the Düzce Watershed and proposes using local biological resources for phytoremediation of contaminated water systems as a model for other areas. It analyzes the Biological Accumulation Factor (BAF) and Translocation Factor (TF) values of readily available aquatic macrophytes to reduce dependence on costly and ecologically risky exotic species. The native-species-first approach proposed here, along with its standardized assessment methodology, would thus render this study's results both valuable and applicable to other areas experiencing similar pressures from pollution. In other words, this paper provides a demonstration that local flora can be efficient in removing pollutants and lays down the groundwork for a nature-based flexible model for sustainable water management.

EXPERIMENTAL

Study Area

The Büyük Melen River which drains this watershed, holds critical importance as it supplies water to the Istanbul metropolis. Düzce Province is located at 40°49′36 North and 31°10′31 East coordinates (Düzce Governorate 2025).

Düzce occupies a strategic position between the two major urban centers of Istanbul and Ankara, serving as a vital transit corridor characterized by extremely high traffic volume. In the years following the 1999 earthquake, this strategic location was further leveraged by both state incentives and individual investments, accelerating and diversifying industrial growth. Currently, the province hosts five large-scale industrial zones along with numerous small-scale enterprises. Primary industrial activities are concentrated in manufacturing and chemical processing, spanning sectors from metal-machinery and automotive to textiles and forest products (Koç *et al.* 2025b; Düzce Governorate 2025). Collectively, this diverse industrial profile encompasses numerous sectors capable of creating a significant pollution footprint. As a result, the province experiences a quickly expanding population that now surpasses 400,000. The region features a heterogeneous landscape comprising both agricultural and industrial land uses. However, the combination of intense industrial activity, heavy vehicular emissions, and demographic pressure has resulted in substantial environmental impacts. The province's topography intensifies this condition: Düzce lies within a bowl-shaped basin encircled by mountain ranges, a configuration that markedly limits air movement and natural ventilation. This geomorphological arrangement hinders pollutant dispersion, resulting in their entrapment above the city. Düzce is recognized as one of Türkiye's most polluted cities, and, in the 2021 World Air Pollution Report, it was ranked among the top five most polluted cities in Europe (Pulatoğlu *et al.* 2025).

Industrial, urban, as well as agricultural activities within the province create a high potential for heavy metals to be deposited into its river systems and wetlands. Sampling sites (see Fig. 1) were taken from the main river of Düzce Province-Büyük Melen River- and its tributaries (Küçükmelen River: S1, S2; S3, S4; Asar River: S5, S6; Uğursuyu River: S7, S8) as well as from Efteni Lake (Sites S9 -S13)-an important wetland for this province. The land use characteristics surrounding the sampling stations exhibit substantial variation across the watershed. Upstream stations on the Küçük Melen and Uğursuyu rivers (S1, S3, S7) predominantly lie within forested regions with minimal anthropogenic disturbance. In contrast, the Asar Stream sampling points traverse the urban center of Düzce (S5), positioned in close proximity to industrial zones (textile, metal, and forest products) and the D-100 highway (S6), a major conduit for traffic-related pollutants. Downstream stations (S2, S4, S8) and Efteni Lake (S9–S13) are largely encircled by intensive agricultural lands, where the application of fertilizers and pesticides is common, effectively acting as a watershed sink.

Sampling sites were determined by first identifying pollution points due to industrial and urban discharges, then collecting samples upstream from these points together with collecting samples downstream from them. Therefore, two samples were taken for each tributary of the river before and after the pollution source. Additionally, five different points in Efteni Lake were sampled (Fig. 1).

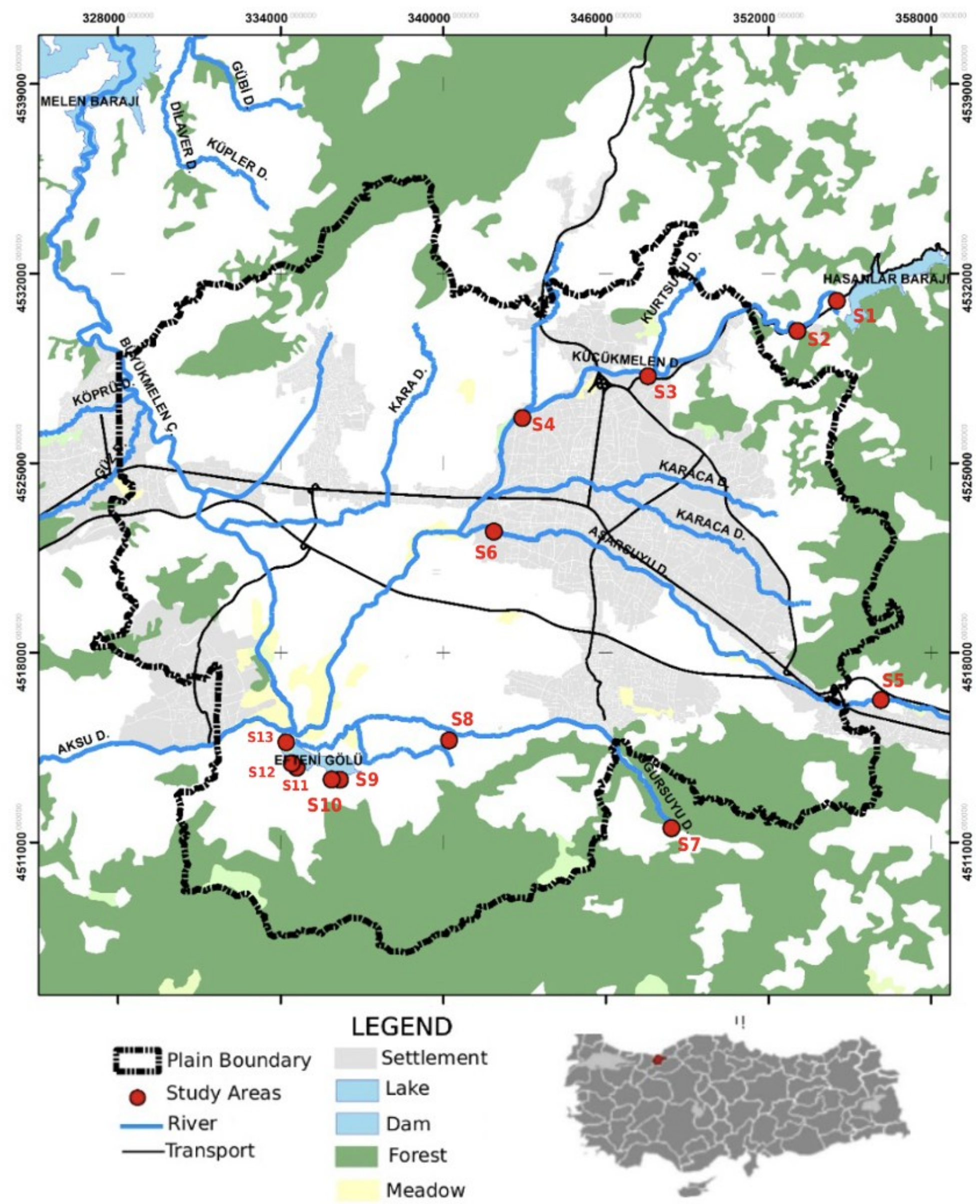

Fig. 1. Study area; Küçükmelen River (S1-S2, S3-S4), Asar River (S5-S6), Uğur River (S7-S8), Efteni Lake (S9-S10-S11-S12-S13)

Water, Plant, and Sediment Sampling

The study was based on monthly water sampling. Thus, a total of 12 water samples were collected from each sampling point over the period of one year. During the water sample collection, water temperature (°C) and pH were determined *in situ* using a Hach HQ40d multi-parameter device. Water samples were collected by immersing the sampling bottles to about 15 cm depth below the river surface with their mouths directed against the water flow (Chapman 1996). Other measurements were conducted on these samples, which were transported to the laboratory in 500-mL polyethylene containers at +4 °C under cold chain conditions.

Vegetation assessment at the prescribed sampling sites aimed to determine dominant species utilizing the Braun-Blanquet (1932) abundance-coverage framework. In total, 41 plant specimens representing 19 species across 15 families were collected for analysis (see Table 1). To ensure representativeness, each plant sample was composed of at least three healthy individuals sampled from the same station. Samples were separated into root and stem/leaf components following Kalra (1998). In parallel, three replicate bottom-sediment samples were collected from a depth of 0 to 15 cm in the immediate vicinity of the plant habitats, as described by Chapman (1996). All chemical analyses were conducted in triplicate to confirm measurement precision.

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Table 1. Plant Species Found in the Sediments of the Rivers and Efteni Lake

Family	Taxon Name	Family	Taxon Name
Alismataceae	*Alisma plantago-aquatica* L.	Onagraceae	*Epilobium hirsutum* L.
Asteraceae	*Bidens tripartita* L.	Plantaginaceae	*Plantago major* L.
Ceratophyllaceae	*Ceratophyllum demersum* L.		*Veronica anagallis-aquatica* L.
Cyperaceae	*Cyperus longus* L.	Poaceae	*Echinochloa crus-galli* (L.) P. Beauv.
Lamiaceae	*Lycopus europaeus* L.		*Paspalum distichum* L.
	Mentha pulegium L.		*Phragmites australis* (Cav.) Trin. ex Steud.
Lemnaceae	*Lemna minor* L.	Polygonaceae	*Polygonum amphibium* L.
Lentibulariaceae	*Utricularia australis* R.Br.	Trapaceae	*Trapa natans* L.
Lythraceae	*Lythrum salicaria* L.	Typhaceae	*Typha latifolia* L.
Nymphaeaceae	*Nymphaea alba* L.		

Analysis of Samples

An analysis was performed on the concentrations of seven heavy metals that are commonly measured in all water, sediment, and plant samples. These include Cu, Cd, Cr, Fe, Ni, Pb, and Zn. The plant samples taken from the sampling areas were separated into two parts: roots (below-ground parts) and shoots (above-ground parts including stems and leaves). They were then dried in a laboratory at 105 °C before being ground. A sample weighing between 0.15 to 0.25 g had 6 mL of HNO_3 (65%) and 2 mL of H_2O_2 (30%) added to it for incineration by microwave digestion. This solution was made up to 40 mL with ultra-pure water afterward. It was also filtered through filter paper in preparation for processing. Sediment samples were dried in an oven at 40 °C and passed through a 0.5-mm sieve; then, a sample weighing 0.2 g had 10 mL of aqua regia solution added to it and was brought up to volume with ultrapure water to 50 mL The solution was filtered through filter paper in preparation for processing. Heavy metals totally dissolved from the water samples were digested using a microwave system by adding 6.25 mL of HNO_3 (65%) and 2 mL of H_2O_2 (30%). The solution was then diluted to 40 mL with ultra-pure water. If particulate matter is present, it is filtered using filter paper. Analyses were performed using an Inductively Coupled Plasma-Optical Emission Spectrometer (ICP-OES) device (Optima 2100 DV; PerkinElmer, Shelton, CT, USA). The instrument was operated in Dual View mode using standard argon plasma conditions recommended by the manufacturer.

Statistical Analysis

Statistical analysis and data visualization were performed using the R programming software. Univariate analysis of variance (ANOVA) was employed to assess pollution status and seasonal variation in rivers and Efteni Lake. The ANOVA was also utilized to evaluate heavy metal contamination in plant and sediment samples. For detected statistical differences, Duncan's multiple range test ($p < 0.05$) was applied for intergroup comparisons (Kabacoff 2011).

Sediment-to-Plant Transfer Factor (BAF): The BAF was defined as the ratio of an element's concentration in the plant to its concentration in the sediment, reflecting the degree of transfer from sediment to plant (Eid *et al*. 2020).

$$BAF = \text{Root Element Concentration/ Sediment Element Concentration (mg/kg)} \quad (1)$$

Translocation Factor (TF) Between Roots and Stems: The TF was defined as the ratio of an element's concentration in the stem to its concentration in the roots, indicating the efficiency of translocation from roots to aerial parts (Eid *et al*. 2020).

$$TF = \text{Stem Element Concentration/ Root Element Concentration (mg/kg)} \quad (2)$$

RESULTS AND DISCUSSION

Changes in pH, Temperature, and Heavy Metal Concentrations in Rivers and Efteni Lake

pH assessment in water

The average minimum at Efteni Lake was found to be 8.74 and a maximum of 9.09 upstream (Table 2). These values are above the upper limit of 8.5 for Class I waters as per the Surface Water Quality Regulation (TSWQR, 2015), which means that the rivers in Düzce Watershed have slightly alkaline characteristics. The statistical evaluation indicated that this difference between measurement points is significant ($p < 0.05$). The lower pH value of Efteni Lake than other points can be attributed to biological and chemical processes occurring within it (Kullberg *et al.* 1993). Seasonal changes in water pH values were also assessed within the study scope. The highest pH value was measured during spring months, with an average of 9.11, while the lowest one, averaging 8.79, was detected during winter months (Table 3). Statistical analysis determined that this difference was significant as well ($p < 0.05$). An increase in photosynthetic activities during spring months probably consumed carbon dioxide from the water, which increased the pH level; its decrease during winter months could be attributed to enhanced decomposition activities and release of carbon dioxide back into the water (Wetzel 2001).

Evaluation of water temperature

Water temperature was measured to range between an average of 16.38 °C (upstream) and 16.94 °C (downstream) at all points with minimal variation. The average temperature of Efteni Lake was taken as 16.85 °C (Table 2). This shows that there was no significant difference in temperature between stations, which indeed also came out from statistical analysis wherein no significant difference between measurement points could be established ($p > 0.05$). The major change in value happened seasonally; naturally, it would be expected to have the highest measurement during summer months at a reading of 25.90 °C and the lowest during winter months at a reading of 8.82 °C (Table 3). Statistical evaluation confirmed that this difference between seasons was highly significant ($p < 0.05$), which is an expected outcome considering the climatic characteristics of the area and the seasonal cycle concerning sunshine duration (GDM 2025). However, water temperature can directly influence heavy metals dissolution and precipitation balances, chemical reaction rates, and metabolic activities within an aquatic ecosystem (Kabata-Pendias 2010).

Evaluation of Cd concentration in water

The concentrations of Cd were noted as a minimum of 0.0041 mg/L at the downstream and a maximum of 0.0045 mg/L in Efteni Lake. Concentrations of Cr, Pb, and other metals generally remained below the national and international regulatory limits (limit values are provided in Table 2). However, Cd levels consistently exceeded these standards. These values significantly exceed the legal limit of 0.0002 mg/L established by the TSWQR. It can, therefore, be stated that the Düzce Watershed river system poses an extremely hazardous condition with regard to cadmium content. However, there were no statistically significant differences between spatial locations for measurement points ($p > 0.05$). The primary reason for having such high levels in Efteni Lake is likely attributable to excessive use of phosphorus-based fertilizers in nearby agricultural areas as reported by Öktüren Asri *et al.* (2007). Seasonal variations in Cd concentration have been found to be statistically significant ($p < 0.05$). The highest value was measured in spring at 0.0091 mg/L and the lowest value was measured in autumn at 0.0012 mg/L (Table 3). This increase during spring may be due to leaching from snowmelt, rains, and increased agricultural activities. Moreover, some geochemical conditions, such as dissolved organic matter in water and low pH, can enhance the solubility of Cd by desorbing it from the sediment (Tipping 2002; He *et al.* 2016). The relatively high concentrations during summer months may be due to concentration pollutants because of reduced river discharge, confirming that seasonal hydrological effects determine pollution dynamics (Nyantakyi *et al.* 2019).

Assessment of Cr concentration in water

The Cr concentrations at the sampling sites and in Efteni Lake varied between 0.0041 mg/L at the site of introduction and 0.0047 mg/L in the lake (Table 2). These values were much lower than the limit given by Surface Water Quality Regulation (0.02 mg/L), which means that there is no danger from Cr pollution in this study area, as indicated by the statistical difference between measurement points ($p > 0.05$). Seasonal variation of Cr values in water was also assessed. The maximum value was recorded during the spring at 0.0091 mg/L, while during the autumn it dropped to a minimum of 0.0015 mg/L (Table 3); this difference turned out to be statistically significant (p <0.05). Cr can be found in water due to industrial activities such as production, metal plating, and tanning leather (Radojević and Bashkin 2006). Increased transport of chromium into water bodies from these possible sources during the spring rains could account for observed seasonal variations (Singh *et al.* 2011; Alloway 2013).

Assessment of Cu concentration in water

The concentration of Cu was determined as a minimum value of 0.0058 mg/L upstream and a maximum value of 0.0066 mg/L downstream (Table 2). All of these values are well below the limit given in the TSWQR, which is 0.02 mg/L, showing that the rivers in Düzce Watershed do not create a hazard with respect to copper contamination. There was no significant difference between the measurement points as revealed by statistical evaluation (p >0.05). Seasonal variations of copper levels were also assessed, and it was found that the highest level of copper was measured during the spring months at 0.0081 mg/L, while the lowest was measured during the autumn months at 0.0046 mg/L (Table 3). This difference, however, was significant in terms of statistical evaluation (p <0.05). The most likely reason for this increase is that surface runoff from agricultural lands and urban areas increases with snowmelt plus the rains during the spring months (Alloway 2013). Dissolved organic matter, hardness, and pH content are water quality parameters that significantly influence copper toxicity (De Schamphelaere and Janssen 2002). Even though low total copper values have been measured, toxic effects on aquatic organisms can be seen under low pH conditions.

Assessment of Fe concentration in water

Fe concentration ranged from a minimum of 0.037 mg/L in Efteni Lake to a maximum of 0.093 mg/L at the downstream station (Table 2). These values were less than the limit prescribed by TSWQR (0.3 mg/L); hence, it may be concluded that there is no significant risk of Fe contamination in waters of the study area. No significant difference was observed between the measurement points in statistical evaluation (p >0.05). When examined seasonally, the highest concentration was found in winter with a value of 0.177 mg/L and the lowest in spring with a value of 0.004 mg/L (Table 3). The difference between seasons was statistically significant (p <0.05). This might be due to increased rainfall during winter months resulting in high soil leaching which increases iron concentrations; decreased biological activity and oxygen level within water during winter months might keep iron soluble (Hem 1985; Çelebi and Kılıç 2014). Such sudden and localized peaks would be more easily explained by seasonal changes in groundwater levels or surface runoff from iron-rich deep soil layers after heavy rainfall than by an industrial discharge event (Varol and Şen 2012). Generally, increases of Fe in water are related to increases of surface runoff after rains at certain seasons and its interaction with groundwater or release processes from sediments. High Fe concentrations may adversely affect organoleptic properties of water (taste, color) and also may create problems in drinking water treatment (WHO 2017).

Assessment of Ni concentration in water

Ni was recorded at a minimum of 0.0047 mg/L upstream and a maximum of 0.0050 mg/L downstream (Table 2). All of these values are very much below the concentration limit set by the TSWQR (0.02 mg/L) meaning no risk in terms of Ni. Statistical analysis did not show any significant difference between measurement points ($p > 0.05$). Seasonal variation in Ni has also been assessed. The highest level of Ni was recorded in spring at 0.0087 mg/L and the lowest level was found in autumn at 0.0022 mg/L (Table 3). Statistical analysis deemed this difference as significant ($p < 0.05$). Therefore, it can be interpreted that more rainfall and surface runoff during the spring season tend to carry mobilized Ni both from natural geological structures and from soil accumulated anthropogenic sources, such as fossil fuel combustion, industrial emissions, and agricultural activities into water systems (Czemiel Berndtsson 2014).

Assessment of Pb concentration in water

Pb concentrations in Efteni Lake ranged from 0.0058 to 0.0081 mg/L downstream (Table 2). These values approach, yet do not surpass, the limit specified for Class I waters in the TSWQR (0.0012 mg/L). This suggests a potential risk, particularly near pollutant sources. Statistical analysis, however, revealed no significant differences among sampling sites ($p > 0.05$), implying a diffuse distribution of Pb input across the region (Zhang *et al.* 2022). Seasonal assessment showed the highest concentrations in summer (0.0120 mg/L) and spring (0.0115 mg/L), with the lowest value in winter (0.0014 mg/L) (Table 3). The seasonal differences were statistically significant ($p < 0.05$). This pattern may be attributed to reduced river discharge during summer, which concentrates pollutants, and to the transport of Pb accumulated on roadside and urban surfaces from exhaust emissions into the water *via* rainfall in the spring (Smith 1976; Adachi and Tainosho 2004; Wolfand *et al.* 2022).

Assessment of Zn concentration in water

Zn concentration ranged from 0.0054 mg/L at the downstream to 0.0065 mg/L in Efteni Lake (Table 2). These values were much lower than the TSWQR limit of 0.2 mg/L, which means that Düzce rivers do not pose any risk regarding Zn contamination. There was no statistically significant difference between the measurement points ($p > 0.05$). The maximum value found in Efteni Lake is believed to come from some pesticides and fertilizers used on adjacent agricultural lands (Wang *et al.* 2022). When Zn values were assessed by season, it was determined that the highest concentration was in spring at 0.0096 mg/L and the lowest concentration was in autumn at 0.0032 mg/L (Table 3). This difference between seasons has been found statistically significant ($p < 0.05$). It is known that this increase in Zn level corresponds with the beginning of agricultural activities in spring together with enhanced rainfall, which triggers surface runoff (Wolfand *et al.* 2022). The common occurrence of Zn in animal manure and certain formulations of pesticides makes it easier for these agricultural inputs to enter water systems through surface runoff during rainy times (Nicholson *et al.* 2003). Moreover, urban roofing materials and galvanized surface corrosion products can join with rainwater and raise Zn levels (Karlen Wallinder *et al.* 2001). Indeed, as Seven *et al.* (2018) observed, agricultural and industrial activities greatly contribute to increasing soil and water Zn levels.

Overall, agricultural activities contribute to the elevated heavy metal loads observed in spring; however, these seasonal peaks are also significantly influenced by surface runoff following heavy rainfall, which transports traffic-derived particulates and atmospheric deposits into the aquatic system (Sevik *et al.* 2019; Wolfand *et al.* 2022).

Table 2. Heavy Metal Concentrations in Rivers Upstream, Downstream and in Efteni Lake Waters

Sampling Area	pH*	Temp. (°C)	Cd (mg/L)	Cu (mg/L)	Pb (mg/L)	Fe (mg/L)	Zn (mg/L)	Ni (mg/L)	Cr (mg/L)
Upstream	9.09 ± 0.25a	16.38 ± 7.46a	0.0042 ± 0.005a	0.0058 ± 0.004a	0.0070 ± 0.008a	0.0703 ± 0.16a	0.0056 ± 0.006a	0.0047 ± 0.0049a	0.0042 ± 0.0055a
Downstream	9.04 ± 0.22a	16.94 ± 7.74a	0.0041 ± 0.006a	0.0066 ± 0.003a	0.0081 ± 0.010a	0.0931 ± 0.23a	0.0054 ± 0.004a	0.0050 ± 0.0048a	0.0041 ± 0.0056a
Efteni Lake	8.74 ± 0.40b	16.85 ± 6.96a	0.0045 ± 0.005a	0.0064 ± 0.004a	0.0058 ± 0.007a	0.0367 ± 0.10a	0.0065 ± 0.006a	0.0048 ± 0.0048a	0.0047 ± 0.0058a
TSWQR	6.5 - 8.5	25	0.0002	0.02	0.0012	0.3	0.2	0.02	0.02
*: Values indicated by different letters in the columns are significantly different at the α: 0.05 confidence level									

Table 3. Seasonal Variation in Heavy Metal Concentrations in Rivers and Efteni Lake Waters

Sampling Area	pH*	Temp. (°C)*	Cd (mg/L)*	Cu (mg/L)*	Pb (mg/L)*	Fe (mg/L)*	Zn (mg/L)*	Ni (mg/L)*	Cr (mg/L)*
Winter	8.79 ± 0.33a	8,82 ± 2,08a	0.0019 ± 0,004a	0.0054 ± 0.004a	0.0014 ± 0.004a	0.1768 ± 0.286a	0.0054 ± 0.006a	0.0033 ± 0.003a	0.0020 ± 0.003a
Spring	9.11 ± 0.22b	18.54 ± 4.32b	0.0091 ± 0,007b	0.0081 ± 0.004b	0.0115 ± 0.011b	0.0038 ± 0.011b	0.0096 ± 0.005b	0.0087 ± 0.005b	0.0091 ± 0.006b
Summer	8.85 ± 0.43a	25.90 ± 2.46c	0.0051 ± 0,006c	0.0071 ± 0.004b	0.0120 ± 0.009b	0.0340 ± 0.098b	0.0054 ± 0.006a	0.0052 ± 0.006c	0.0050 ± 0.006c
Autumn	9.02 ± 0.28b	13.66 ± 5.07d	0.0012 ± 0,007a	0.0046 ± 0.004a	0.0026 ± 0.002a	0.0429 ± 0.094b	0.0032 ± 0.004a	0.0022 ± 0.007a	0.0015 ± 0.002a
*: Values indicated by different letters in the columns are significantly different at the α: 0.05 confidence level									

Table 4. Heavy Metal Concentrations in Sediments Taken from Efteni Lake, Upstream, Downstream Contamination

Sampling Area	Cu (mg/kg)*	Pb (mg/kg)*	Fe (mg/kg)*	Zn (mg/kg)*	Ni (mg/kg)*	Cr (mg/kg)
Upstream	11.9 ± 4.3a	17.2 ± 29.9a	15840 ± 3799a	33.6 ± 8.3a	31.4 ± 28.7a	34.5 ± 22.3a
Downstream	15.1 ± 9.7b	0.0 ±0.0b	19487 ± 2918b	41.7 ± 6.4b	33.5 ± 23.9a	35.2 ± 22.5a
Efteni Lake	29.1 ±6.6c	6.7 ± 12.8c	31975 ± 12526c	58.4 ± 27.5c	37.6 ± 14.5b	35.5 ± 20.4a
Limits	50	50	-	150	30	250
*: Values indicated by different letters in the columns are significantly different at the α: 0.05 confidence level						

Table 5. Heavy Metal Concentrations in Plants Growing in Efteni Lake, Upstream, Downstream Contamination

Sampling Area	Cd (mg/kg)*	Cu (mg/kg)*	Pb (mg/kg)*	Fe (mg/kg)*	Zn (mg/kg)*	Ni (mg/kg)*	Cr (mg/kg)
Upstream	0.075 ± 0.16a	58.2 ± 113a	1.26 ± 1.81a	5330 ± 5359a	50.4 ± 34.8a	11.7 ± 10.7a	32.4 ± 65.6a
Downstream	0.096 ± 0.16a	37.9 ± 40.1b	0.64 ± 0.96b	7539 ± 8314b	39.9 ± 15.4b	11.1 ± 10.1a	35.2 ± 32.8a
Efteni Lake	0.146 ± 0.64b	26.7 ± 40.4c	0.08 ± 0.32c	12715 ± 11067c	45.0 ± 33.1c	29.2 ± 42.3b	30.8 ± 22.1a
*: Values indicated by different letters in the columns are significantly different at the α: 0.05 confidence level							

When benchmarked against other major Türkiye watersheds, heavy metal concentrations in the Melen River typically exceed those of pristine rural streams, yet they remain lower than or comparable to levels reported in highly industrialized areas and contaminated watersheds (Varol 2011; Tokatlı *et al.* 2020). Given that the Melen System provides a critical water supply for the Istanbul metropolitan region, even these moderate accumulation trends represent a growing anthropogenic threat that requires ongoing monitoring.

Heavy Metals in Rivers and the Possibility of Remediation Using Phytoremediation Methods

Cu, Cd, Cr, Pb, and Zn are heavy metals that can be very dangerous to the environment in river and wetland systems due to their toxic and bioaccumulative properties. Heavy metals influence plant health and growth and likewise represent substantial hazards to organisms within ecosystems, especially humans, through the food chain. Some non-essential heavy metals are toxic and carcinogenic to humans even at low exposure levels. By contrast, essential micronutrients, though required for biological processes, can exert toxic effects when present at elevated concentrations. (Demirci *et al.* 2026). The majority of pollution with these metals comes from anthropogenic sources related to industrial effluents, agricultural runoff, and mining activities (Zhang *et al.* 2015; Guan *et al.* 2018; Isinkaralar *et al.* 2022). Likewise, Düzce and its surroundings bear witness to the fact that water resources are exposed to danger regarding Cd and Pb in a region where intense industrialization and agricultural activities take place. Indeed, Düzce rivers as well as Efteni Lake are under particular threat for Cd and Pb; thus this situation constantly threatens aquatic life (Jiang *et al.* 2022) and human health (Yi *et al.* 2017) because of the long-term persistence of these metals in sediments.

Phytoremediation is a biological remediation process that can be used as an attempt to reduce the negative impacts of heavy metals. It is based on the principle that these plants could uptake these elements from soil and water environments and store them in their tissues (Haq *et al.* 2020; Tan *et al.* 2023). The distribution of heavy metals between water and sediment phases varied significantly depending on the element. While high concentrations of Fe, Cu, Zn, and Ni in sediments indicated that the sediment was acting as a primary sink for these metals over time (Table 4), Cd exhibited a different behavior. The low Cd levels in sediment, contrasting with its potential risk in the water column, can be explained by geochemical dynamics; specifically, low pH and the presence of dissolved organic matter promote the desorption of Cd from sediment, thereby increasing its solubility in the water phase (Tipping 2002; He *et al.* 2016). Regarding regulatory compliance, the majority of sediment samples remained within the limits established by the Türkiye Ministry of Environment and Forestry (2010). For instance, Cu concentrations (11.9 to 29.1 mg/kg) were well below the regulatory limit. Similarly, Pb values (maximum 17.2 mg/kg) did not exceed the limit. However, a notable exception was observed at the Beyköy station, where Ni concentrations (approx. 35 mg/kg) exceeded the legal limit of 30 mg/kg (see Table 4 footnotes for specific limit values). This specific elevation is attributed to the local geological structure, which contains ultramafic rocks naturally rich in Ni and Cr, indicating a geogenic origin (Kabata-Pendias and Mukherjee 2007; Keskin 2018).

Heavy metal uptake and accumulation in plants arise from complex, multifactorial processes rather than a single determinant. The primary determinants include physicochemical properties of the growth medium, such as pH, organic matter content, and redox potential, which directly influence metal speciation and bioavailability (Kabata-

Pendias 2010). Furthermore, biological factors inherent to the plant, such as species-specific physiological mechanisms, root morphology, and growth stage, play a critical role in absorption efficiency (Ali *et al.* 2013; Balliu *et al.* 2021). Additionally, external anthropogenic factors, particularly traffic density and distance to pollution sources, significantly affect metal accumulation levels depending on the plant organism and exposure pathway (Sevik *et al.* 2019). Consequently, the variations in metal concentrations observed in this study can be attributed to the synergistic effects of these geochemical, biological, environmental, and demographic variables.

The pronounced localized concentration of Pb at the Asar 1 station indicatively points to a particular anthropogenic source. It is well documented that emissions from vehicles and the abrasion of automotive components release Pb into the environment, after which it can be conveyed to aquatic systems *via* surface runoff (Sevik *et al.* 2019; Czemiel Berndtsson 2014). The Asar stream flows in close proximity to the D-100 (Ankara-Istanbul) highway, which is characterized by extremely high traffic volume. Consequently, the elevated Pb concentrations observed at this station are attributed to the transport of accumulated traffic-related pollutants into the river system through surface runoff. Although Cu and Zn concentrations are within legal limits at the present time, relatively high values around Efteni Lake indicate agricultural activities compounded with urban surface runoff together with industrial impacts on this region (EPA 2025).

Although river waters exhibit relatively low heavy metal concentrations, substantial accumulations of heavy metals were detected in plant tissues (Bai *et al.* 2018). The substantial metal content observed, despite low instantaneous concentrations in the water, reflects the ongoing uptake and bioaccumulation capacity of these species over time, thus corroborating their function as effective biological sinks (Eid *et al.* 2020; Sojka and Jaskula 2022). These aquatic macrophytes assimilate metals *via* multiple pathways: directly from the water column through submerged leaves and stems, from sediments *via* roots, and through atmospheric deposition on aerial foliar surfaces (foliar uptake) (Sevik *et al.* 2019). The substantial removal efficiency exhibited by these aquatic plants can be ascribed to the functional groups, such as hydroxyl and carboxyl moieties, within their cellulosic framework, which serve as effective binding sites for heavy metal ions (Hubbe *et al.* 2011). Given that sediments serve as the primary reservoir for heavy metals, they frequently constitute the main source for plant uptake. Consistent with this, the current study found that roots generally accumulate higher metal concentrations than shoots, indicating a primary restriction of metal translocation to aerial tissues (exclusion strategy).

This uptake behavior is further supported by the calculated bioconcentration and translocation factors (BAF and TF), which indicate preferential metal retention in root tissues for most elements, coupled with limited upward translocation. An important exception was Cd, which showed higher concentrations in shoots. This elevated accumulation in aboveground parts implies that Cd exhibits high mobility within the plant vascular system and is efficiently translocated from roots to shoots, underscoring the potential of these species for phytoextraction.

In this framework, the study computed the BAF and TF values to quantify the relative rates at which plant species take up heavy metals from soil and move metals from roots to shoots, respectively. These metrics were calculated separately for each plant species to elucidate the sediment-to-plant and root-to-stem transfer pathways for each heavy metal (Figs. 2 and 3).

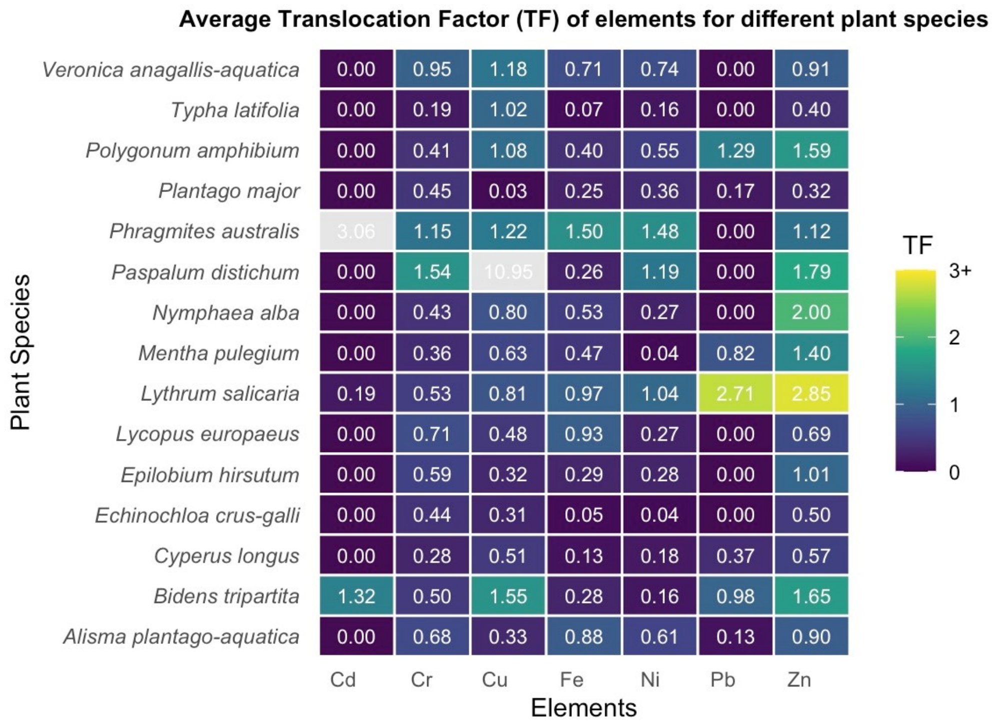

Fig. 2. This figure shows how efficiently plants transport heavy metals absorbed by their roots to their stems. High values (> 1) indicate that the plant is successful in transporting that metal.

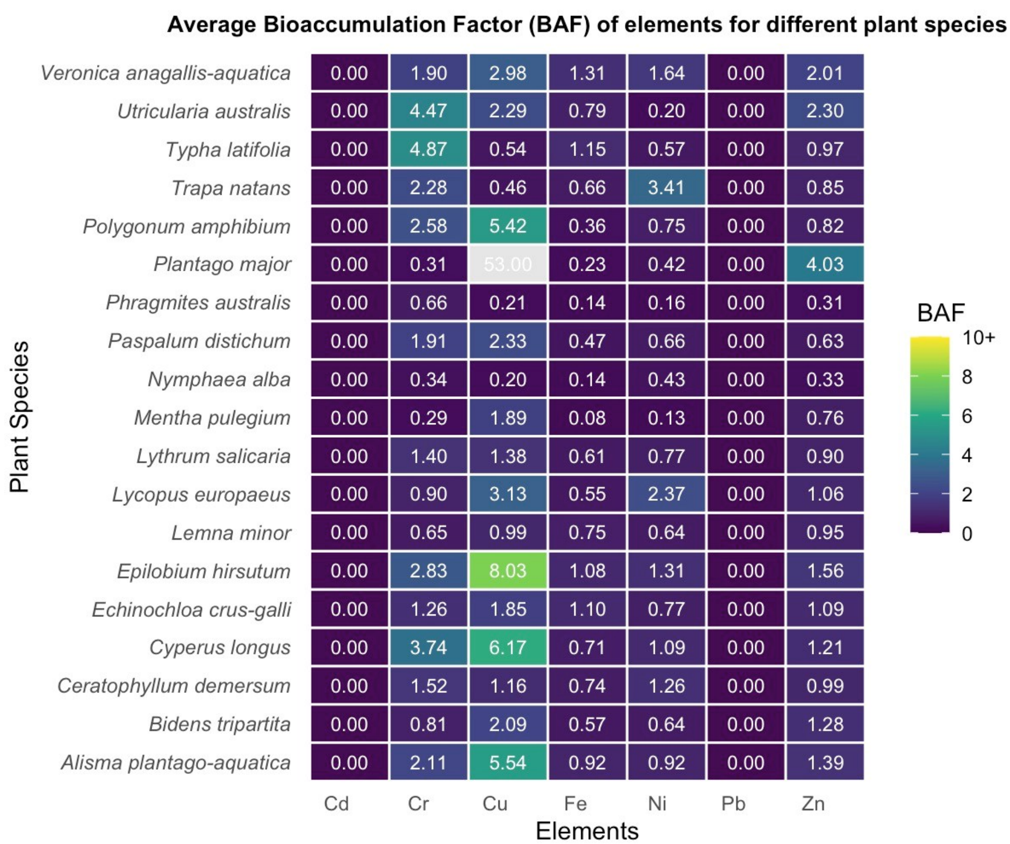

Fig. 3. This figure shows how efficiently plants absorb heavy metals from sediment into their roots. High values (> 1) indicate that the plant is successful in accumulating that metal.

Plants demonstrating a TF greater than 1 show an effective translocation of an element from roots to stems and leaves, indicating potential for phytoextraction (Bader *et al.* 2019). Such species can be employed to remediate contaminated soils by assimilating elements into harvestable above-ground tissues. Consequently, the harvested biomass can be utilized for bioenergy production, thereby contributing to a circular economy (Hou *et al.* 2022). For instance, a TF of 10.95 for Cu in *Paspalum distichum* L. signifies substantial root-to-shoot translocation by the plant. Conversely, plants with TF values below 1 tend to retain elements in their roots, rendering them suitable for phytostabilization because the elements are not accumulated in the aerial parts. Phytostabilization aims to prevent mobilization of soilborne contaminants by immobilizing them within root systems and reducing their dispersion to air or groundwater (Usman *et al.* 2019). As an example, *Cyperus longus* L. exhibits a low TF value of 0.13 for Fe, indicating iron retention in the plant's roots. Accordingly, TF values are pivotal in determining the appropriate remediation strategy-phytoremediation (high TF) or phytostabilization (low TF)-for specific elements across plant species (Eid *et al.* 2020).

Plants with a BAF value greater than 1 are considered to incorporate a target element in their bodies more rapidly than its concentration in the soil/sediment; hence, they can be classified as species with high bioaccumulation potential (Eid *et al.* 2020). The *Plantago major* L. plant was found to have an extremely high BAF value of 53.00 for Cu, which means it efficiently takes up copper from the soil and this makes it a strong candidate for phytostabilization in Cu contaminated sediment. In contrast, *Paspalum distichum* L. also presented high potential with a BAF value of 2.33 for copper.

Plants exhibiting high bioconcentration factor (BAF >1), but low translocation factor (TF <1), are particularly suited to phytostabilization, as they immobilize and accumulate contaminants in their root systems and thereby reduce transfer to the atmosphere or groundwater (Bello *et al.* 2018). For instance, *Cyperus longus* L. demonstrated Cu (BAF = 6.17, TF = 0.51) and *Typha latifolia* L. demonstrated Fe (BAF = 1.15, TF = 0.07), illustrating root-level accumulation with minimal translocation to shoots. This is consistent with evidence from the Nile Delta (*Eid et al.* 2020) and Sultan Marsh in Türkiye (Demirezen and Aksoy, 2004), where *Typha* spp. were reported to function effectively as excluders, predominantly retaining metals within their roots. Moreover, the ability of these genera to remediate environments contaminated with multiple metals is supported by Chandra and Yadav (2011), who showed that related taxa (*Typha* and *Cyperus*) can concurrently remove a broad spectrum of metals from aqueous solutions.

In contrast, species optimal for phytoextraction possess both high BAF and TF values, enabling uptake of metals and subsequent translocation to harvestable aerial parts. *Paspalum distichum* L. exemplified this approach for Cu (TF = 10.95). Meanwhile, certain species, such as *Mentha pulegium* L., exhibited low BAF values for chromium and Ni (0.29 and 0.13, respectively), reflecting an exclusion strategy that limits metal uptake and contributes to reduced soil metal mobility.

Plantago major L. exhibited the greatest potential for Cu hyperaccumulation in its roots, evidenced by a bioconcentration factor (BAF) of 53.0. This suggests a phyto-stabilization strategy, consistent with Galal and Shehata (2015), who reported that this species does not significantly transport heavy metals to its aerial parts (shoots). *Paspalum distichum* L. also demonstrated a notable capacity to translocate the accumulated Cu from roots to shoots, with a TF of 10.95. *Utricularia australis* R.Br. showed the highest Cr accumulation in terms of BAF (4.47), whereas *Paspalum distichum* displayed a substantial ability to transport Cr from roots to shoots (TF = 1.54). *Typha latifolia* uniquely recorded a bioaccumulation value exceeding 1 for Fe with BAF = 1.15. *Lythrum salicaria* was the most efficient species for root-to-shoot iron translocation (TF = 0.97); however, this TF value near 1 also suggests substantial iron sequestration in roots. *Trapa natans* L. accumulated the greatest amount of Ni in soil, as indicated by BAF = 3.41, while *Lythrum salicaria* L. was the most effective Ni transporter (TF = 1.04). For Zn, *Plantago major* L. achieved the highest accumulation efficiency (BAF = 4.03), whereas *Lythrum salicaria* L. showed the greatest Zn translocation capability (TF = 2.85). Regarding Cd and Pb, most plant species displayed low or negligible BAF and TF values, implying limited uptake and/or transport for these metals. The lack of a meaningful BAF for Cd partly reflects the challenge of determining soil Cd concentrations; accordingly, many plants exhibit Cd TF values that are zero or near zero. Nevertheless, due to Cd's high aqueous solubility, some species, such as *Bidens tripartita* L. and *Phragmites australis*, exhibit TF values exceeding 1, indicating that water-based uptake becomes a prominent pathway under elevated aqueous Cd concentrations (Benavides *et al.* 2005). Regarding Pb, most BAF values were near zero, consistent with Pb's tendency to bind to root surfaces or tissues. Nonetheless, *Lythrum salicaria* L. recorded the highest Pb TF (2.71), indicating a notable capacity to transport trace amounts of Pb from roots to shoots.

CONCLUSIONS

1. The greatest accumulation of heavy metal contamination in this study was found in bottom sediments. This occurred primarily because metals emanating from human activities are conveyed through the water column, deposited in sediments, and then build up over time. Cadmium (Cd), which had a concentration that exceeds the national and international water quality standards in the water column, poses an ecological hazard for both sediment biota and water quality.
2. The amounts of heavy metals significantly vary in water and sediment samples, and then they build up in aquatic plants with specific differences between plant types as well as between part of the plant.
3. *Plantago major* is efficient in stabilizing contaminated soils due to its high capability of root accumulation of pollutants. In contrast, *Paspalum distichum* has a high translocation factor for copper from roots to upper tissues and can be classified as an efficient species in the removal of metals from soil by phytoremediation.
4. The functional categorization of the local macrophyte community into strong accumulators (*e.g.*, *Plantago major*), effective transporters (*e.g.*, *Paspalum distichum*), and robust stabilizers (*e.g.*, *Mentha pulegium*) provides a sustainable, nature-based framework for the remediation of degraded aquatic ecosystems and broader ecological restoration.
5. High biomass capacity species, such as *Phragmites australis*, along with easily harvestable aquatic plants, such as *Utricularia australis*, have the potential for both phytoremediation and bioenergy production by effectively accumulating metals within their biomass. The ash produced by the controlled combustion of these plants biomass for energy generation is enriched with elements, creating a manageable resource for metal recovery or safe disposal. Thus, this integrated approach, which combines the removal of pollutants from the environment, clean energy production, and metal

recovery within one system, constitutes an effective means of sustainable environmental management while directly upholding the tenets of the circular bioeconomy.

6. Phytoremediation should be considered as a practical alternative solution, particularly in cases of widespread contamination and in developing regions. Accordingly, when both technical feasibility and economic advantages are considered, phytoremediation technologies can be considered among the priority choices within the scope of sustainable environmental management.
7. Given that the Melen River Watershed constitutes a crucial water supply for the Istanbul metropolitan region, the observed heavy metal accumulation trends – driven by seasonal runoff and escalating anthropogenic pressure – necessitate integrated management strategies extending beyond local remediation. The native aquatic plants identified in this study present a viable, environmentally sustainable approach to mitigating these risks prior to their impact on public health.

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Conflict of Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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